Structural Templating in a Nonplanar Phthalocyanine Using Single Crystal Copper Iodide

Luke A. Rochford, Alexandra J. Ramadan, Dean S. Keeble, Mary P. Ryan, Sandrine Heutz, and Tim S. Jones*

Structural templating is a well-established method to influence the morphologies and structures of organic semiconductor thin films and therefore control their electronic and physical properties.[1–4] As such both inorganic and organic thin films have been employed as structural templating layers to improve device parameters.[5–7] Copper (I) iodide (CuI) has shown recent promise as an evaporable templating layer for small molecule photovoltaic applications.[8] Our recent work has revealed the structure of highly crystalline films of CuI and their effects on subsequently deposited thin films of planar and nonplanar metal phthalocyanines (MPcs).[9–11] When prepared as a thin film at ambient and elevated substrate temperatures we have shown that CuI adopts a (111) orientation on amorphous SiO_2, which promotes a substrate parallel molecular plane in planar MPc molecules.[9] Those data were obtained on CuI (111) layers which exhibit a high degree of orientation in the out-of-plane direction, but in-plane orientation is essentially random. The limitation of such disordered systems has been demonstrated by the observation of two polymorphs in iron phthalocyanine layers grown at high temperature on microstructured films of CuI. In that work, the presence of {100} crystal planes on the exposed sides of dispersed (111) oriented crystallites was responsible for the observed behavior.[10] Therefore, the most ideal system in which to study the effect of the individual crystal surfaces upon growth of thin films is an appropriately oriented single crystal.

In this paper, we present the growth of CuI crystals from solution which have large faces corresponding to the (111) crystal plane of the CuI single crystal structure.[12] These high surface quality crystals are employed as substrates for growth of vanadyl phthalocyanine (VOPc) and unlike previously reported work (where multiple distinct orientations were measured) only one crystallographic orientation is observed.

Dr. L. A. Rochford, Prof. T. S. Jones
Department of Chemistry
University of Warwick
Gibbet Hill Road, Coventry CV4 7AL, UK
E-mail: l.rochford@warwick.ac.uk
A. J. Ramadan, Prof. M. P. Ryan, Dr. S. Heutz
Department of Materials
Imperial College London
Exhibition Road, London SW7 2AZ, UK
Dr. D. S. Keeble
Diamond Light Source
Harwell Science and Innovation Campus
Fermi Ave, Didcot, Oxfordshire OX11 0QX, UK

DOI: 10.1002/admi.201400540

Preparation of CuI single crystals was undertaken to avoid the limited grain size and random in-plane orientation in previously presented CuI thin films. The crystals exhibited hexagonal or triangular habit from slow growth in saturated acetonitrile solution (**Figure 1**a). This is indicative of expression of threefold or sixfold planar symmetry in the top faces of these crystals suggestive of (111) orientation. For surface analysis by low energy electron diffraction (LEED), crystals were mounted on Ta sample plates and loaded into UHV where diffraction patterns were collected without any surface preparation. LEED showed a hexagonal arrangement of spots consistent with a 1×1 (111) pattern with no additional spots at lower energies (Figure 1b). Additionally, X-ray diffraction (XRD) patterns were recorded (in ambient conditions) after careful alignment to the surface normal of the crystal and only {111} reflections were observed (Figure 1c). Atomic force microscopy (AFM) images (collected in ambient air) showed that the top faces were flat with 60° rotational symmetry in their step edge arrangement (**Figure 2**a, b). The combination of these experimental observations established that the crystals are of high quality and possess large exposed (111) top surfaces.

Thin films (50 nm thickness) of VOPc were prepared on these surfaces by evaporation at elevated substrate temperature (T_{sub} = 155 °C). To determine if growth at this temperature resulted in any changes to the CuI single crystal, a control experiment was performed in which the crystal was annealed for 1 h at growth temperature. The resulting LEED pattern was unchanged suggesting no change in the surface crystal structure (Figure S1, Supporting Information) in agreement with previous high-temperature structural studies.[13] The crystal structure and surface morphology of the resultant VOPc films were analyzed using XRD and AFM, respectively. Diffraction patterns (**Figure 3**a) exhibit only a single peak which can be indexed as $(1\bar{3}\bar{2})$ using the VOPc single crystal structure and is the only feature differentiating the VOPc/CuI pattern from that of the bare CuI (111) crystal. In order to ascertain whether a single orientation of VOPc was present, Rietveld refinement was undertaken on the VOPc/CuI XRD data. The CuI and VOPc were both fitted with March–Dollase preferred orientation with a March factor of 0.001 (corresponding to 99.9% orientation) around the CuI (111) and VOPc $(1\bar{3}\bar{2})$ directions, respectively (Figure S2, Supporting Information).[14,15] The lack of any other peaks (even those with higher structure factors) which would be expected from the isotropic VOPc powder pattern confirms a singly oriented film. The $(1\bar{3}\bar{2})$ plane of the VOPc structure corresponds to a molecular orientation in which the ligand plane of the molecule is normal to the surface as demonstrated in Figure 3b.

ADVANCED MATERIALS INTERFACES
www.advmatinterfaces.de

Materials Views
www.MaterialsViews.com

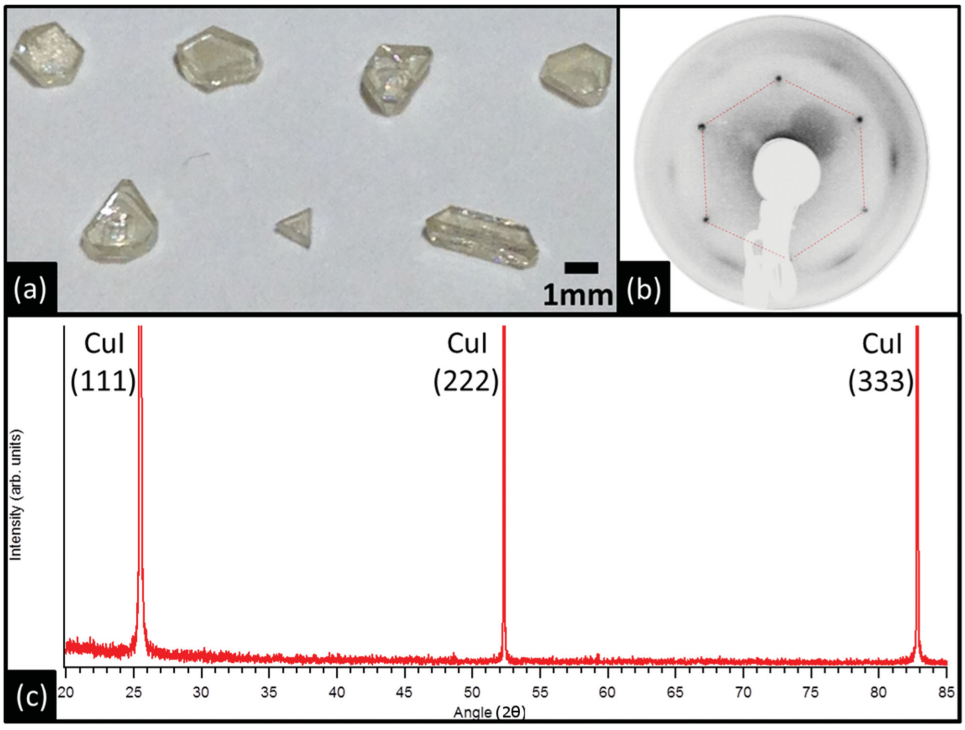

Figure 1. a) Photograph showing the solution grown (111) oriented CuI crystals, b) a representative LEED pattern (electron beam energy of 62 eV) with a hexagonal guide-to-the-eye and c) XRD patterns.

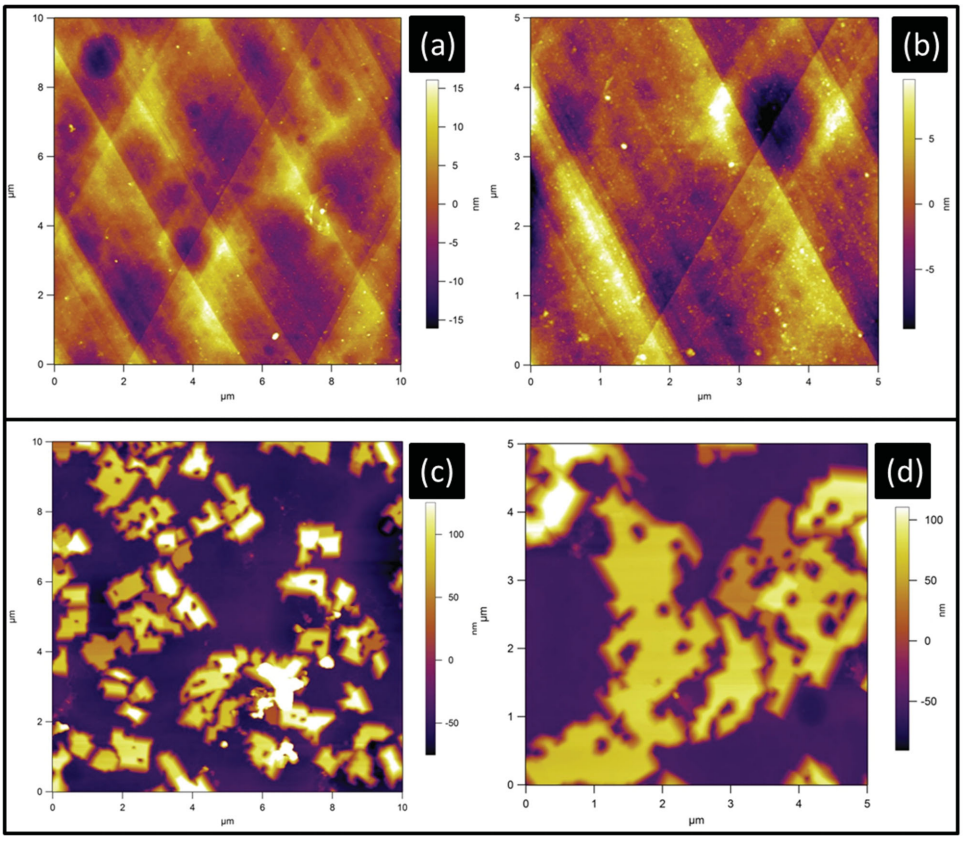

Figure 2. AFM images showing the a,b) CuI crystal surface and c,d) a 50 nm VOPc/CuI thin film grown at a surface temperature of 155 °C.

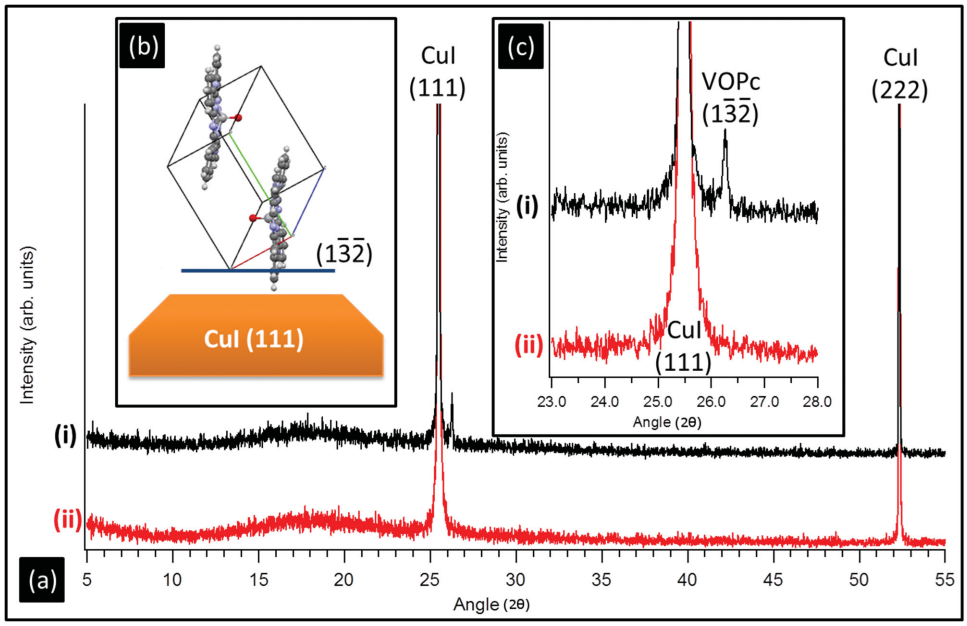

Figure 3. a) An XRD pattern of 50 nm (i) VOPc/CuI (111) and (ii) the bare CuI crystal along with c) an expanded view around the (111) peak. A schematic of the inferred molecular orientation with respect to the crystal surface is presented in (b).

Images of the VOPc/CuI film from AFM (Figure 2c,d) show isolated island morphology consistent with a Volmer–Weber growth mode.[16] Crystallites show combinations of square symmetry in their projected shape; each edge is close to orthogonal to the nearest neighbor. In contrast to the AFM images acquired in recent work on high-temperature templating of VOPc, only one crystallite morphology is observed in the region imaged in these experiments.[11] Although not exhaustive in its scope this comparison suggests that the additional morphological features observed in previous images are resultant from additional crystallite orientations. More explicitly, the implication is that differing orientations of VOPc produce islands with different morphologies. The effect of the exposed edges of individual CuI (111) crystallites upon a phthalocyanine overlayer has also been demonstrated.[10] Together these observations imply that the grain boundaries and other macroscopic defects in polycrystalline thin films promote alternative orientational configurations which in turn lead to the additional peaks in XRD patterns of VOPc on oriented polycrystalline substrates. These data are highly suggestive of the promotion of a single molecular orientation in the VOPc overlayer by the single crystalline CuI (111) surface.

High surface quality CuI crystals were synthesized from solution and characterized using a combination of imaging and diffraction techniques, revealing (111) oriented plate-like crystal morphology. These single-crystal surfaces were then employed as substrates for the growth of thin films of the nonplanar molecule VOPc. Clear differences in morphology and crystal structure were observed in comparison to previously published results employing polycrystalline CuI (111) films on amorphous SiO_2 substrates. The origin of these differences is interpreted as the lack of grain boundaries in the single-crystal substrate, which intrinsically had in-plane and out-of-plane order, and the proposition that the (111) oriented CuI single crystals are a more suitable model system for the CuI (111) surface. Only a single peak is observed in the corresponding XRD pattern which suggests only a single molecular orientation with respect to the substrate plane in the thin film. These observations allow a deeper understanding of the templating interaction between the molecular film and the underlying CuI (111) crystal surface.

Experimental Section

Copper iodide (98% pure, Sigma-Aldrich, UK) was used to create saturated solutions in hot (60 °C setting on a Corning PC-420D hotplate) acetonitrile without further purification. These solutions were filtered using 0.22 μm (MILLEX DURAPORE) PVDF syringe filters and placed in a Pyrex crystallizing dish covered with Parafilm which was pierced at a single point with a syringe needle to allow solvent vapor to escape. This assembly was placed on a laboratory hotplate set at 60 °C in a vibration-free environment and allowed to rest for 168 h. This produced CuI crystals which are pictured in the main text which and were mounted to Ta sample plates (using a minimum amount of Ag-loaded epoxy) for use in UHV. Photographic images were captured using an Apple iPhone 5c "smartphone" with a graduated calliper as scale guide. VOPc (85% pure, Acros Organics, BE) was triply purified by thermal gradient sublimation[17] and the resulting crystals were used for growth from a UHV evaporation cell (Karl Eberl GmbH) at 370 °C at a rate of 0.3 Å s^{-1}. VOPc films were grown with an elevated substrate temperature (T_{sub} = 155 °C) in a custom built multichamber UHV system with a base pressure better than 3×10^{-10} mbar. The substrate temperature was measured using a K-type thermocouple mounted close to the sample and calibrated using an optical pyrometer. LEED patterns were collected with a SPECTALEED (Omicron) rear-view MCP-LEED with nanoamp primary beam current. Images of these patterns were captured using a digital CCD camera interfaced to a personal computer. Thin film XRD patterns were obtained using a Panalytical X'Pert Pro MRD diffractometer with monochromatic Cu $K\alpha_1$ radiation. Atomic force microscopy (AFM) images were recorded using an MFP-3D (Oxford Instruments Asylum Research, Santa Barbara, USA) in AC mode (tapping mode) using Olympus AC240-TS silicon tips.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

L.A.R. and A.J.R. contributed equally to this work. A.J.R. and S.H. acknowledge support from the Engineering and Physical Sciences Research Council (EPSRC), UK (Grant No. EP/G037515/1). M.P.R. thanks the EPSRC for the award of Grant No. EP/J500161/1. L.A.R. and T.S.J. acknowledge support from the EPSRC, UK (Grant No. EP/H021388/1). The Panalytical MRD diffractometer used in this research was obtained through the Science City Advanced Materials Project: Creating and Characterizing Next Generation Advanced Materials, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

Received: December 5, 2014
Revised: February 24, 2015
Published online: April 1, 2015

[1] B. Verreet, R. Müller, B. P. Rand, K. Vasseur, P. Heremans, *Org. Electron.* **2011**, *12*, 2131.
[2] K. Vasseur, K. Broch, A. L. Ayzner, B. P. Rand, D. Cheyns, C. Frank, F. Schreiber, M. F. Toney, L. Froyen, P. Heremans, *ACS Appl. Mater. Interfaces* **2013**, *5*, 8505.
[3] S. Heutz, C. Mitra, W. Wu, A. J. Fisher, A. Kerridge, M. Stoneham, A. H. Harker, J. Gardener, H.-H. Tseng, T. S. Jones, C. Renner, G. Aeppli, *Adv. Mater.* **2007**, *19*, 3618.
[4] W. Wu, L. A. Rochford, S. Felton, Z. Wu, J. L. Yang, S. Heutz, G. Aeppli, T. S. Jones, N. M. Harrison, A. J. Fisher, *J. Appl. Phys.* **2013**, *113*, 013914.
[5] P. Sullivan, T. S. Jones, A. J. Ferguson, S. Heutz, *Appl. Phys. Lett.* **2007**, *91*, 233114.
[6] C. H. Cheng, J. Wang, G. T. Du, S. H. Shi, Z. J. Du, Z. Q. Fan, J. M. Bian, M. S. Wang, *Appl. Phys. Lett.* **2010**, *97*, 083305.
[7] S. Heutz, R. Cloots, T. S. Jones, *Appl. Phys. Lett.* **2000**, *77*, 3938.
[8] B. P. Rand, D. Cheyns, K. Vasseur, N. C. Giebink, S. Mothy, Y. Yi, V. Coropceanu, D. Beljonne, J. Cornil, J.-L. Brédas, J. Genoe, *Adv. Funct. Mater.* **2012**, *22*, 2987.
[9] L. A. Rochford, D. S. Keeble, O. J. Holmes, G. J. Clarkson, T. S. Jones, *J. Mater. Chem. C* **2014**, *2*, 6056.
[10] L. A. Rochford, A. J. Ramadan, S. Heutz, T. S. Jones, *Phys. Chem. Chem. Phys.* **2014**, *16*, 25404.
[11] A. J. Ramadan, L. A. Rochford, D. S. Keeble, P. Sullivan, M. P. Ryan, T. S. Jones, S. Heutz, *J. Mater. Chem. C* **2015**, *3*, 461.
[12] M. Gu, P. Gao, X.-L. Liu, S.-M. Huang, B. Liu, C. Ni, R.-K. Xu, J. Ning, *Mater. Res. Bull.* **2010**, *45*, 636.
[13] D. Keen, S. Hull, *J. Phys.: Condens. Matter* **1995**, *7*, 5793.
[14] E. Zolotoyabko, *J. App. Crystallogr.* **2009**, *42*, 513.
[15] W. A. Dollase, *J. Appl. Crystallogr.* **1986**, *19*, 267.
[16] S. R. Forrest, *Chem. Rev.* **1997**, *97*, 1793.
[17] A. R. McGhie, A. F. Garito, A. J. Heeger, *J. Cryst. Growth* **1974**, *22*, 295.